International Journal of Applied, Physical and Bio-Chemistry Research (IJAPBCR)
ISSN(P): 2277-4793; ISSN(E): 2319-4448
Vol. 5, Issue 1, Aug 2015, 1-10

• Journal Publications • Research Consultancy

INFLUENCE OF ALKALI CONCENTRATION ON COMPLETE CONVERSION OF FLY ASH IN TO A FRAMEWORK ALUMINOSILICATE UTILIZING ALKALINE HYDROTHERMAL SYNTHETIC METHODOLOGY

HEMA KUNDRA[1] & MONIKA DATTA[2]

Department of Chemistry, University of Delhi, Delhi, India

ABSTRACT

Coal is one of the most commonly used fuel and remains the least expensive of all the fossil fuels for the generation of electricity. In the process of generating electricity utilizing coal, large quantities of coal combustion by-products (CCPs) are generated. More than 60% of the total non-combustible residual particles resulting from the coal combustion processes in thermal power plants are fly ash. In India fly ash is being generated at the rate of about 60 million tons per annum (MTPA) from about 75 thermal power plants and is expected to increase to 100 MTPA by the turn of the century. Low amount of beneficial nutrients, low cation exchange capacity, high alkalinity, the presence of toxic metal ions in fly ash and high transport cost for relatively low value product are some of the factors responsible for the limited utility of fly ash. To overcome these difficulties many technologies have been developed for gainful utilization of fly ash . India records a very low percentage of 15-20% of fly ash as compared to a corresponding figure for developed countries. With this in view, the possibility of synthesizing high value products such as zeolites from fly ash was explored.

KEYWORDS: Coal, Fly Ash, Waste Utilization, Zeolite, Value Added Products

INTRODUCTION

World net electricity generation is expected to increase by 77% from 2006-2030 and coal continues to fuel the largest share of worldwide electric power generation [1], with total hard coal consumption of 5522 MT (million tons) [2]. India is currently the third largest producer of coal in the world, after China and the United States with a production of about 407 million tons (MT) of hard coal. In India the demand for coal for power plants has rapidly increased. About 80% of the coal produced in the country was utilized for power generation in 2006–07 and is projected to increase upto 5 folds in 25 years. [4].Other key coal consumers are steel and cement industries [3, 4]. India has the fourth largest reserves of coal in the world and will maintain its position for another 40-50 years [4]. Present electricity generation capacity is 143 Gega watts and expected to increase to 800 Gega watts by the year 2032.

Indian coal is generally of poor quality in terms of high ash content (ranging from 30-35%), high moisture content (ranging from 4-20%), low calorific value (between 2500-5000 kcal/kg) and high amounts of toxic trace elements especially mercury (Hg) [4-6]. The low calorific value leads to more use of coal for the generation of same amount of electricity. In India, about 70% power plants are coal based [5, 7] generating more than 160 million tones of fly ash annually. Because of the increase in the electricity generation, there is consistent increase in the requirement of coal leading to an increased production of fly ash [5, 8].

Therefore, there is a need to encourage research on the development of materials using fly ash through novel synthetic methodologies. Many technologies have been developed for gainful utilization of fly ash such as it is use as a bottom layer in road construction, concrete and ceramic production, in building industries and also as backfills. About 5-6% of total fly ash is used up in the above mentioned applications, and rest of it is disposed off. Current conventional means for fly ash disposal by converting them into slurry are both inadequate and wasteful, since they entail long term financial and land problems. When fly ash is not properly disposed, it is known to pollute air, water and soil. It causes various respiratory problems when inhaled and lowers the yield when it settles on crops and leaves. Thus future fly ash disposal means presents economic and environmental problems [7, 9].

Several attempts have been made for proper utilization of fly ash either to reduce the cost of disposal or to minimize its impact on environment [10]. For the last few years there has been much interest in zeolites. Since fly ash contains more than 80% silica and alumina, therefore it can serve as the raw material for synthesis of zeolites and appears to be one of the most promising alternatives as it has emphasis on value addition to waste material [10, 11].

High cation exchange capacity, high surface area and variable pore size are some of the special features of zeolites which make them versatile materials for targeting wide range of applications e.g., materials for soil remediation and enhancement of plant growth, catalysts for chemical and petrochemical industries, adsorbents and ion exchangers in a variety of processes such as water softening and in the separation and removal of gases. Other applications are in agriculture, animal husbandry and construction [12]. Several research reports have been published on synthesis of zeolites [13] (P, A, X, Y, analcime, chabzite etc.) using various synthetic procedures [10, 14-28]. However, these attempts are beset with drawbacks of low crystallinity, low yield, residual fly ash in the product and mixture of zeolites in product. Thus, the present study is aimed at developing a cost effective, synthetic methodology for conversion of a waste (fly ash) into a technologically important and a value added single product zeolite/s.

EXPERIMENTAL

Materials

In the present investigation, fly ash sample was procured from National thermal Power Plant, India and sodium hydroxide (AR, 98%) Pure, was procured from Qualigens, India. The aluminosilicate from fly ash was synthesized by the modification of the reported procedure **[18].**

Synthesis

In order to convert fly ash into a value added product, the complete dissolution of the fly ash, in the form of a gel, has been done by heating the alkali fly ash mixture. After the formation of the gel, the solution was kept for ageing step (close to the room temperature) followed by the curing /crystallization step as per the reported literature. 5g of fly ash sample was taken; fly ash sample was sieved to eliminate larger particles. The fly ash was added to sodium hydroxide solution in a conical flask to make the slurry and was stirred at various temperatures followed by ageing and curing. The resultant mixture was then cooled to room temperature and then washed several times with double distilled water to eliminate extra alkali followed by drying in oven at 60-70°C for 6-7 hours.

Keeping in mind the need for the synthesis of a value added product and cost effectiveness of the process, effect of parameters such as concentration of alkali was investigated from 1M-3M on the above mentioned method by keeping the entire parameters (initial mixing temperature and time, ageing temperature and time and curing temperature and time)

constant ("Table 1"). In order to verify the reproducibility of the procedure, four batches of samples were synthesized using above mentioned conditions. Each sample was analyzed by all relevant techniques to identify the structure of the synthesized product.

Characterization

Various analytical techniques have been employed for this purpose. To identify crystalline materials in the samples, X-ray diffractograms were recorded on Philips PW3710 X-ray Diffractometer using Cu Kα (alpha) radiations with tube voltage 45 kV and 40 mA with a sampling step of 0.02° and a scan time of 4sec in 2θvalues ranging from 10-70°. Infrared spectroscopic (FT-IR) studies were carried out to identify their structural features. FTIR spectra were taken in KBr on a Perkin Elmer FTIR spectrophotometer. For each sample, spectrum has been recorded for 64 scans with 4cm^{-1} resolution between 4000–400cm^{-1} region. To avoid the interference from the CO_2 and water, IR chamber was flushed with dry nitrogen. Morphology of fly ash and synthesized product were investigated by using Scanning Electron Microscope (SEM), the SEM analysis has been performed on ZEISS EVO Scanning Electron Microscope Model EVO 50. Thermal stability was investigated by thermo gravimetric (TGA) methods. TGA was recorded on Shimadazu DTG 60 at a heating rate of 30°C/min upto 700°C and a flow rate of 100mL/min.

RESULT AND DISCUSSIONS

X-Ray Diffraction Studies

The X-ray powder diffraction patterns ("Figure 1" a, b, c and d) of fly ash (S-01) and the synthesized products (S-02, S-03 and S-04) indicate the conversion of fly ash to crystalline aluminosilicates. A relatively broad band centered at 2θ = 26.2° is the characteristic feature of class F fly ash (glassy phase) having relatively low calcium content ("Figure 1" a) **[29, 30]**. The presence of sharp peaks at 2θ=16.34(5.41), 30.81(2.89), 33.11(2.70), 35.12(2.55), 39.13(2.29), 40.73(2.21), 60.50(1.52) and at 2θ=20.77(4.27), 36.79(2.44), 49.99(1.82), indicates the presence of predominantly mullite ($3Al_2O_3.2SiO_2$) and quartz (SiO_2) respectively, as the crystalline material (JCPDS no. 15-0776 and 05-0490). The halo pattern in the background between 2θ=10.2° and 2θ=40.2° indicates the presence of amorphous material **[31]**. Appearance of increasing amount of crystalline phase/material with the increasing concentration of alkali and the disappearance of diffraction peaks of fly ash ("Figure 1" b-d) is indicative of gradual increase in the extent of conversion of fly ash in to crystalline aluminosilicate. The diffraction pattern has been found to be in good agreement with hydroxysodalite structure **[32-36]**.

Fourier Transformed Infrared Spectroscopic Studies

The FTIR spectra ("Figure 2"a, b, c and d) of fly ash (S-01) and the synthesized products (S-02, S-03 and S-04) indicate the conversion of fly ash to crystalline aluminosilicates. The presence of quartz and mullite as evident from the presence of peak at 1096cm^{-1} and 470cm^{-1}("Table 2") **[37]**. The strongest band appears at 995, 995 and 989cm^{-1} in case of the synthesized product S-02, S-03 and S-04 respectively ("Figure 2" b-d, "Table 3"**)**. This observed shift towards lower wave number with increasing alkali concentration indicates the presence of more number of Al^{+3} into the frame work. Three well-defined medium intensity bands at 718, 696, 661cm^{-1} and the bands at 463 and 434 cm^{-1} has been observed for the S-04 sample ("Figure 2"d) and are in good agreement with the bands reported in the literature for hydroxysodalite structure **[38-43]**. Appearance of increased intensity bands at the same frequencies with increasing alkali concentration suggests the formation of same product.

Scanning Electron Microscopic Studies

Scanning electron micrographs of the fly ash (S-01) and the corresponding synthesized products (S-02, S-03and S-04) indicates the conversion of fly ash to crystalline aluminosilicates ("Figure 3"). Spherical particles with smooth surface have been observed for the fly ash ("Figure 3"a) **[31]**. Deformation of the smooth spherical surface has been observed when fly ah was treated with 1M alkali ("Figure 3"b). Decrease in particle size and the appearance of sharp edges on the surface is clearly seen in case of S-03 sample ("Figure 3"c) suggesting higher conversion of fly ash in to the crystalline material. In case of S-04 sample ("Figure 3"d), a well-defined cubic morphology indicates the complete conversion of fly ash in to a crystalline product. The XRD, FTIR data is also supportive of this observation.

Thermo Gravimetric Studies

Thermo grams of fly ash and the synthesized product ("Figure 4" a, b, c and d) indicate the conversion of fly ash to crystalline aluminosilicates. In case of fly ash ("Figure 4"a) first weight loss of 0.2% is observed in the temperature range of 35-200°C (corresponding to the loss of physically adsorbed water) followed by a weight loss of 1.8% in the temperature range of 200-550°C (attributed to the decomposition of hydrated salts such as Ca $(OH)_2.xH_2O$, $CaSO_3.xH_2O$, etc. present in fly ash). In the temperature range of 550-700°C 0.8% weight loss (attributed to the loss due to the oxidation of unburnt carbon and decomposition of metal carbonates in fly ash) has been observed **[44, 45]**. Two step weight losses in each case were observed for the samples S-02, S-03and S-04. The first step, 30°C to 100°C, amounts to a loss of 4%, 7% and 3.2% , corresponds to the loss of physically adsorbed water. The second step, 100°C to 250°C, amounting to a loss of 4%, 4%, and 4.6% for S-02, S-03and S-04 respectively ("Figure 4" b-d), corresponds to the loss of metal bound water and water located in zeolitic cavity **[46]**.

The total percentage of weight loss in case of fly ash has been relatively very small (2.8%) due to non-framework structure. The presence of cavities and voids in the framework is responsible for the retention of relatively large amount of water.

CONCLUSIONS

From the characterization studies of fly ash and the alkali modified fly ash, it is concluded that complete conversion of fly ash to crystalline, single product (zeolite) has been achieved and it has been found **that the best product is obtained with 3M NaOH as the initial concentration of alkali. The structure was found to have cubic hydroxysodalite type structure.** Present process formulated here for the synthesis of zeolite from fly ash has the advantages of conservation of raw materials cost effectiveness, technically convenient, economical and non-tedious process, high value utilization and partially solving the fly ash disposal problem. So, the outcome of the proposed research work would lead to a cleaner and healthier environment.

ACKNOWLEDGEMENTS

We express our sincere thanks to the following persons for providing instrumentation and other facilities to Department of Chemistry, University of Delhi, Dr. S. C. Datta, IARI, PUSA for extending XRD facility, AIIMS for extending the SEM facility, UGC for the financial support, NTPC for providing the fly ash samples, Dr. Shreedhar, IICT, Hyderabad for extending Solid State MAS NMR facility.

REFERENCES

1. International Energy Outlook (2009). Energy Information Administration. Retrieved from http://www.eia.doe.gov/oiaf/ieo/index.html.
2. Coal Facts (2008). World coal institute. Retrieved from http://www.worldcoal.org,
3. A.P. Chikkatue (2008). A resorce and technology assessment of coal utilization in India. Coal Initiative Report, 1-52
4. R. K. Sachdev (15-17 May 2007). Clean coal technologies-Indian scenario. 3rd International conference on lean coal technologies for our future
5. S. R. Michalski et al (2001). Ash Disposal-Mine Fires-Environment: An Indian Dilemma. Bulletin of Engineering Geology and the Environment, 60, 23–29
6. Provisional Coal Statistics, Coal Controller Organization, Government of India, Ministry of Coal, (2007-2008).
7. Parisara, Envis Newsletter, Utility bonanza from dust, State Environment Related Issues (2007). 2(6), 1-8
8. U.Bhattacharjee et al (2002). Potential of Fly ash Utilization in India . Energy, 27, 151-166
9. H.A.Foner et al (1999). Characterization of Fly Ash from Israel with Reference to its Possible Utilization.Fuel, 78, 215-223
10. S.Hernandez et al (2002). Zeolitic Material Synthesized from Fly ash: Use as Cationic Exchanger. Journal of Chemical Technology and Biotechnology,77,299-304
11. S.S. Rayalu et al (2001). Highly Crystalline Zeolite-A from Fly ash of Bituminous and Lignite coal Combustion. Journal of hazardous Materials, 88 (1), 107-121
12. www.bza.org/zeoltes.html
13. L.R.G. Araújo et al (1999). Synthesis of Cubic Y Zeolite Using a Pulsed Microwave Heating System. Materials Research, 2 (2), 105-109
14. S.Rayalu et al (2000). Highly Crystalline Faujasitic Zeolites from Fly ash. Journal of Hazardous Materials B, 77, 123-131
15. X.Querol et al (2002). Synthesis of Zeolites from Coal Fly ash:An Overview.International Journal of Coal Geology, 50, 413-423
16. N.Murayama et al (2002).Mechanism of Zeolite Synthesis from Coal Fly ash by Alkali Hydrothermal Reaction. International Journal of Mineral Processing, 64, 1-17
17. V.Berkgaut et al (1995). Cation Exchange Properties of Hydrothermally Treated Coal Fly ash. Environmental Science and Technology, 29, 1748-1753
18. H.L.Chang et al (1996). Conversion of Fly ash into Zeolites for Ion-Exchange Applications. Materials Letters, 28, 263-268
19. J.Chen et al (2006). Removal of Phosphate from Aqueous solution by Zeolite Synthesized from Fly ash. Journal

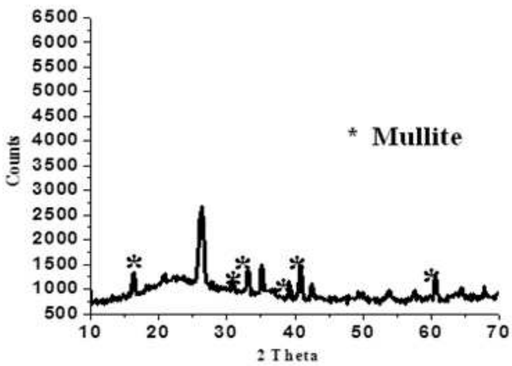
of Colloid and Interface Science, 300, 491-497

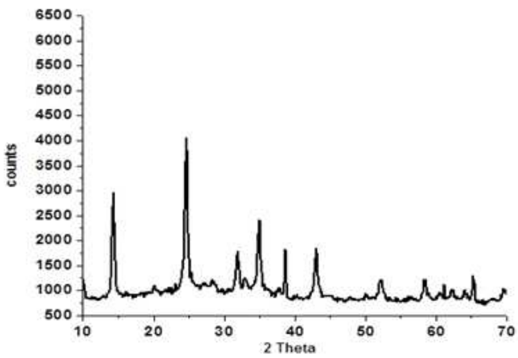
20. S.Furusawa et al (2002). Synthesis,Characterization and Formation Process of Na-X Zeolite from Coal Fly ash. Journal of Materials Synthesis and Processing, 10(3), 43-148
21. K.S.Hui (2006). Effects of Step-Change of Synthesis Temperature on Synthesis of Zeolite 4A from Coal Fly ash. Microporous and Mesoporous Materials, 88, 145-151
22. M.Miyake (2002). Resource Recovery of Waste Incineration Fly ash:Synthesis of Zeolites A and P. Journal of American Ceramic Society,85 (7), 1873-1875
23. K.Ojha et al (2004). Zeolite from Fly ash: Synthesis and Characterization. Bulletin of Material Science, 27(6), 555-564
24. K.Petrus et al (2000). The use of a Modified Fly ash As an Adsorbent for Lead. Water SA, 26(4), 531-536
25. C.Poole et al (2004). A Comparative Study Using Two Methods to Produce Zeolites from Fly ash. Minerals Engineering, 17, 167-173
26. S.Sang et al (2006). Synthesis of Small Crystals Zeolite NaY. Materials Letters, 60, 1131-1133
27. V.S.Somerset et al (2005). Alkaline Hydrothermal Zeolites Synthesized from High SiO_2 and Al_2O_3 Co-disposal Fly ash Filtrates. Fuel, 84, 2324-2329
28. V.Somerset et al (2005). Alkaline Hydrothermal Conversion of Fly Ash Filtrates into Zeolites 2: Utilization in Wastewater Treatment. Journal of Environmental Science and Health,40, 1627-1636
29. S.Diamond (1983). On the Glass Present in Low-Calcium and In High-Calcium Fly ashes. Cement and Concrete Research, 13 (4), 459-464
30. A.R.Brough et al (2001). Adiabatically Cured,Alkali-activated Cement-based Waste forms Containing High Levels of Fly ash Formation of zeolites and Al-substituted C-S-H. Cement and Concrete Research, 31, 1437-1447
31. F.Blanco et al (2005). Variation in Fly ash Properties with Milling and Acid Leaching. Fuel, 84, 89-96
32. K.Katsuki et al (2007). Effect of Anion Species from Ca-sources on Framework Type of Na–Ca Zeolites Prepared at 80℃. Journal of Porous Materials, 14, 401-407
33. M.Alkan et al (2005). The Effect of Alkali Concentration and Solid/Liquid Ratio On The Hydrothermal Synthesis of Zeolite Na-A from Natural Kaolinite. Microporous and Mesoporous Materials, 86, 176-184
34. J.Felsche et al, (1986). Crystal Structures of The Hydro-Sodalite $Na_6[AISiO_4]_6.8H_20$ and of the anhydrous sodalite Na_6 $[AISiO_4]_6$. Zeolites, 6, 367-372
35. M. M. J. Treacy and J. B. Higgins (2001). Collection of Simulated XRD Powder Patterns for Zeolites. Published on behalf of the Stucture Commision of the International Zeolite Association, IV Edition
36. D.W. Breck (1974). Zeolite Molecular Sieves: Structure, Chemistry and Use. John Willey & Sons, A Wiley Inter-science Publication
37. M.Criado et al (2007). Alkali Activation of Fly ash: Effect of The SiO_2/Na_2O Ratio Part I: FTIR study.

Microporous and Mesoporous Materials, 106, 180-191

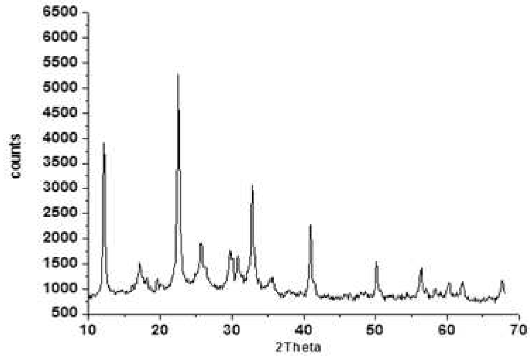
38. Th.Perraki et al (2004). Mineralogical Study of Zeolites from Pentalofos Area,Thrace,Greece. Applied Clay Science, 25, 9-16
39. W.Mozgawa et al (2001).The Relation between Structure and Vibrational Spectra of Natural Zeolites. Journal of Molecular Structure, 596, 129-137
40. H.Zhao et al (2004). Alteration of Kaolinite to Cancrinite and Sodalite by Simulated Hanford Tank Waste and its Impact on Cesium Retention. Clay and Clay Minerals, 52 (1), 1-13
41. D.Zhao et al (1998).Characteristics of The Synthetic Heulandite-clinoptilolite Family of Zeolites. Microporous and Mesoporous Materials, 21, 371-379
42. A.F.Jiménez et al (2005). Mid-infrared Spectroscopic Studies of Alkali-activated Fly ash Structure. Microporous and Mesoporous Materials, 86, 207-214
43. P.A.Jacobs et al (1984).Structure and Reactivity of Modified Zeolites, 23-30
44. S.C.Burris et al (2005). Comparison of Heating Losses and Macro Thermogravimetric Analysis Procedures for Estimating Unburned Carbon in Combustion Residues. Energy & Fuels, 19, 1493-1502
45. H.Li et al (1997). Studies of Fly ash Using Thermal Analysis Techniques. Journal of Thermal Analysis, 49, 943-951
46. P.Castaldi et al (2005). Thermal and Spectroscopic Studies of Zeolites Exchanged with Metal Cations. Journal of Molecular Structure, 734, 99-105

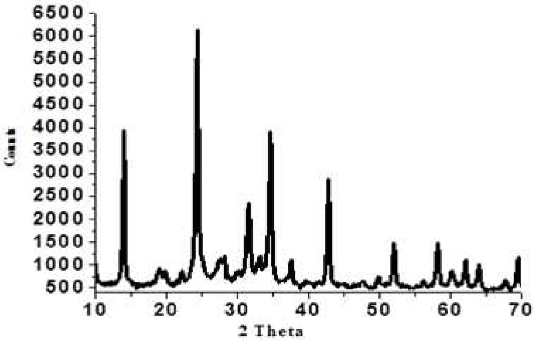
APPENDICES





(a) **(b)**

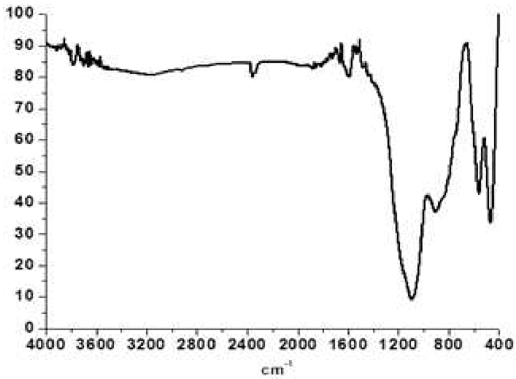


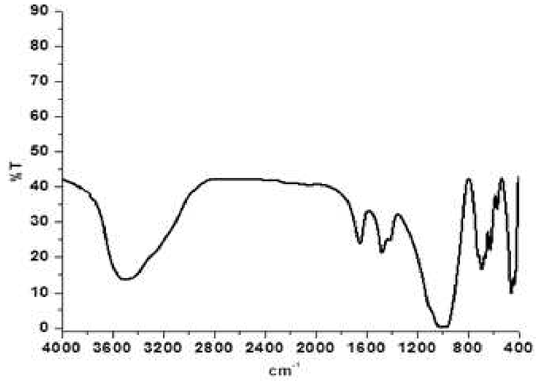


(c)

(d)

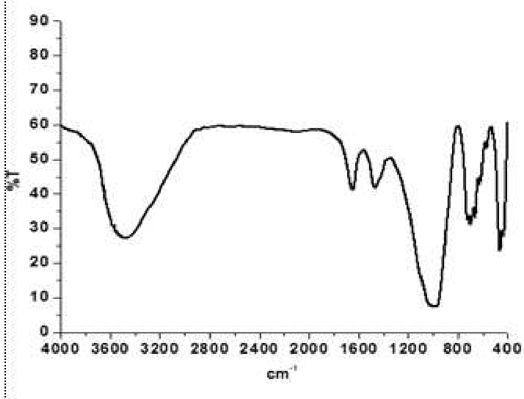
Figure 1: XRD Patterns of Fly Ash and the Product Obtained at Varying Concentration of the Alkali

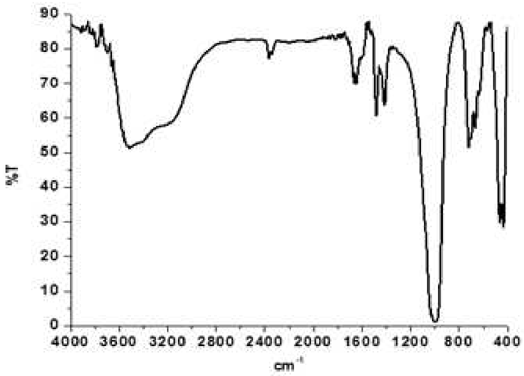




(a)

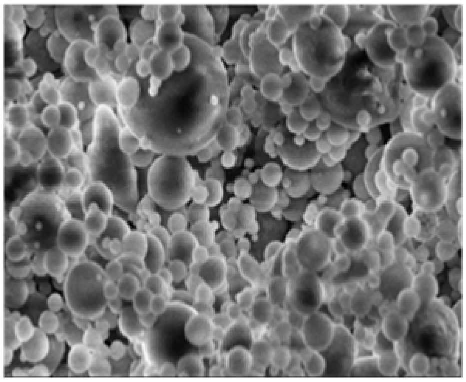
(b)



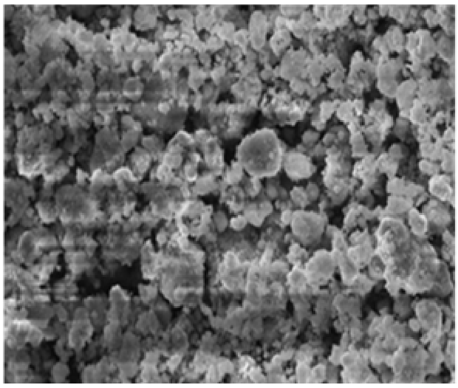


(c) (d)

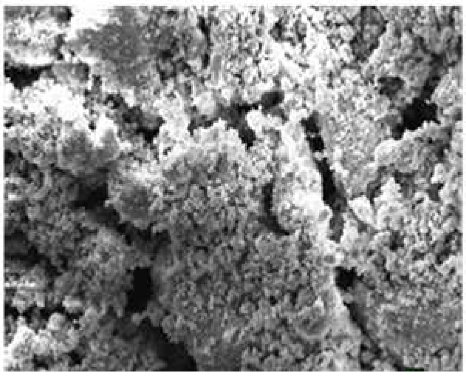
Figure 2: FT-IR Patterns of Fly Ash and the Product Obtained at Varying Concentration of the Alkali



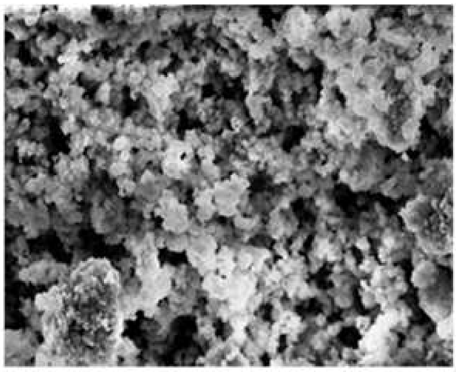
(a)



(b)

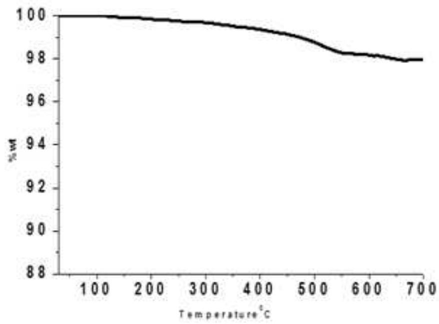


(c)

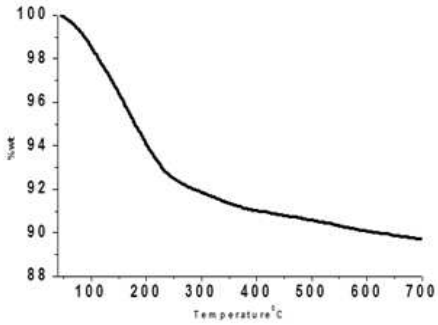


(d)

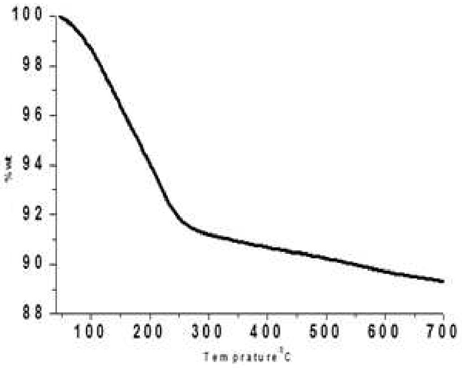
Figure 3: SEM Patterns of Fly ash and the Product Obtained at Varying Concentration of the Alkali



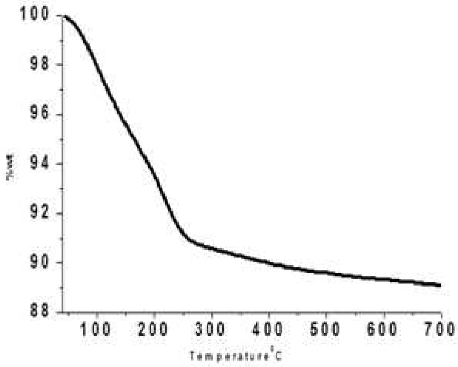
(a)



(b)



(c)



(d)

Figure 4: TGA Patterns of Fly Ash and the Product Obtained at Varying Concentration of the Alkali

Table 1: Variation in the Concentration of Alkali

Product Code	Concentration of Alkali	Initial Mixing		Ageing		Curing	
		Temp.	Time	Temp.	Time	Temp.	Time
S-02	1M	80°C	48	30°C	48	40°C	72
S-03	2M	80°C	48	30°C	48	40°C	72
S-04	3M	80°C	48	30°C	48	40°C	72

Table 2: Vibrational Frequencies of Fly Ash

Vibrational Frequencies (cm^{-1})		Assignments
Observed Values	Reported Values	
1096(s), 906(sh)	1135-1080	Si/Al-O, Asym. Sretching Quartz & Mullite
Broad Shoulder	792-700	Si/Al-O, Sym. Sretching Quartz & Mullite
560 (s), 458(s)	560-550, 460	Si/Al-O, Bending Mullite, Quartz